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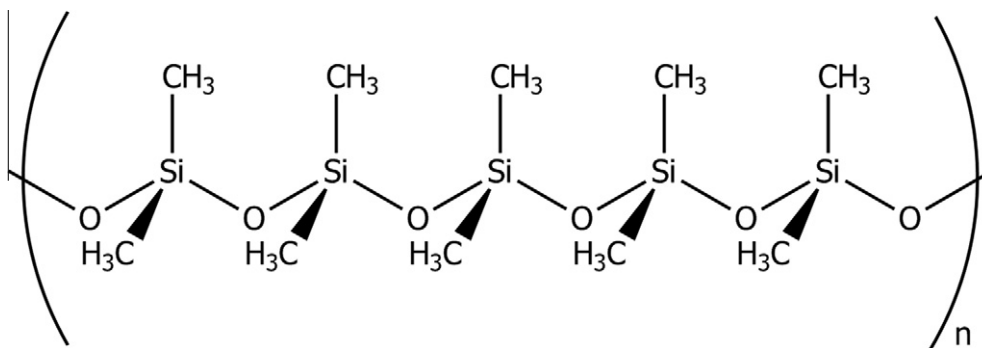
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Graphical abstract

Direct e-beam lithography of PDMS

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J. Bowen, D. Cheneler, A.P.G. Robinson *



Highlights

► We have shown that there are four distinct regimes in the e-beam exposure of PDMS. ► The phase, elastic modulus and resultant thickness are highly dependent on dose. ► In the solid region, the elastic modulus is tuneable by three orders of magnitude.



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Direct e-beam lithography of PDMS

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ABSTRACT

In this paper, the viability of directly exposing thin films of liquid poly(dimethylsiloxane) (PDMS) to electron beam (e-beam) irradiation using e-beam lithographic methods for the purpose of creating permanent micro-scale components has been investigated. By exposing 1.1 μm thickness PDMS films to doses in the range 10–50,000 $\mu\text{C}/\text{cm}^2$, it was discovered that the structure of the resultant film exhibits four distinct phases, depending upon the exposure dose. These phases were manifested in both the resultant Young's modulus and thickness of the developed film. It was found that there is a critical dose whereupon the resultant film undergoes solidification and adheres to the counter surface sufficiently to survive the development process. It has been shown that the Young's modulus of the solid film can be varied over seven orders of magnitude, from that of a viscoelastic material through a rubbery regime to that of a glassy one, by increasing the e-beam dose. At higher doses, excessive backscattering was observed, as well as film swelling, resulting in poor spatial resolution.

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1. Introduction

Poly(dimethylsiloxane) (PDMS) is a versatile material frequently used in the fabrication of micro- and nanoscale devices. It has a unique combination of properties including excellent thermal and chemical stability and non-toxicity making it an attractive material for use in many fields of science, especially in biomedical research [1]. PDMS has a very low glass transition temperature and exists at room temperature in the liquid phase, as a polymer melt. This liquid can be converted into a solid elastomer by cross-linking, a process which is most frequently performed by combining the PDMS with curing agents or catalysts [2]. Generally, the PDMS elastomer is patterned using soft lithography whereby the liquid mixture is poured over a master having relief structure, cured and peeled off [3]. The production of a master and then the PDMS structure is a complicated multi-step process, one that can be greatly simplified by omitting the need of a master by directly patterning the PDMS itself. The most common process for patterning polymers in microengineering is photolithography. PDMS is not photo-sensitive but can be made to be by adding a photoinitiator to the liquid prepolymer [4], although it was found that this method suffers from having relatively low resolution. It has been previously demonstrated that the cross-linking density and mechanical properties of PDMS can be modified by electron beam irradiation [5] and even proton beam bombardment [6]. Its sensitivity to electron radiation [7] has lead to its use as a resist for subsequent

substrate patterning [8] albeit generally in a modified form. These modifications have included replacing the methyl groups with phenyl groups to increase the glass transition temperature [9], the addition of an acid generator during exposure and baking to form silicate glass [10] and the use of a pre-curing agent to solidify the PDMS prior to exposure [11].

e-beam lithography (EBL) is a lithographic technique that is widely used to define nanoscale features and while it is a serial method, the ease of design and resolution [12] means it has great potential in being used to generate a great variety of PDMS-based structures. The chemical composition of PDMS is shown in Fig. 1. During e-beam irradiation, it is hypothesized that methyl groups are removed allowing the backbones of different polymer chains to become cross-linked. However, at large doses, the electrons also can cause chain scission and the formation of other chemical species. Here we introduce the use of EBL as a viable method of directly patterning liquid PDMS to form permanent surface topographies and micro-scale components. To achieve this goal we analyzed the effects of exposing thin liquid films of PDMS to electron radiation in the dose range 10–50,000 $\mu\text{C}/\text{cm}^2$ on the resulting elastic modulus and topography. The data shows that PDMS processed using this method is a viable structural material capable of being utilized in the next generation of microfluidic and other micro devices.

2. Fabrication

PDMS with a zero shear viscosity of 1 Pa s was decanted onto clean Si wafers (IDB Technologies, UK; 2 nm native SiO_2 layer)

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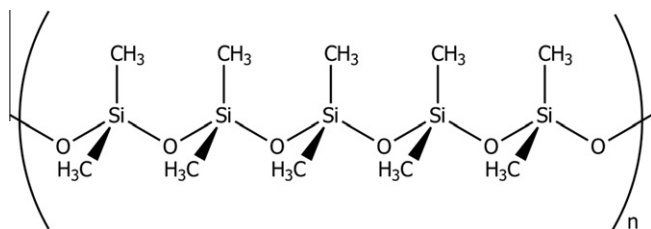


Fig. 1. Schematic of section of PDMS polymer chain.

areas in Fig. 2A and B are due to stage drift after repositioning. Care has been taken to ensure this has not affected subsequent data.

3. Experimental analysis of topography and elastic modulus

Acquisition of topographical and mechanical data were performed using a NanoWizard II AFM (JPK, UK) operating in force scan mapping mode, at a temperature of 18 °C and a relative humidity in the range 25–35%. This involved the use of a scanner with a maximum lateral range of 100 × 100 μm and a maximum vertical range of 90 μm in conjunction with a CellHesion module (JPK, UK). Data acquisition was performed using rectangular 130 μm length Si cantilevers (type NSC36/No. Al, Mikro Masch, Estonia) having pyramidal tips with 10 nm nominal radii of curvature. Cantilever spring constants were on the order 0.2 N/m and were calibrated according to the method reported by Bowen et al. [13]. Mechanical data were acquired at 400 surface locations within the 100 × 100 μm scan area by driving the fixed end of the cantilever at a velocity of 20 μm/s towards the sample surface, whilst monitoring the deflection of the free end of the cantilever using a laser beam. Using JPK Data Processing software, a Hertzian model was fitted to data from four separated positions along the center of each exposed square to assess the mechanical response. A maximum compressive load of 5 nN was applied to the surface during data acquisition, which corresponded to a small indentation strain. Topological data, as exemplified in Fig. 3, was obtained via contact mode AFM imaging, employing a compressive load of

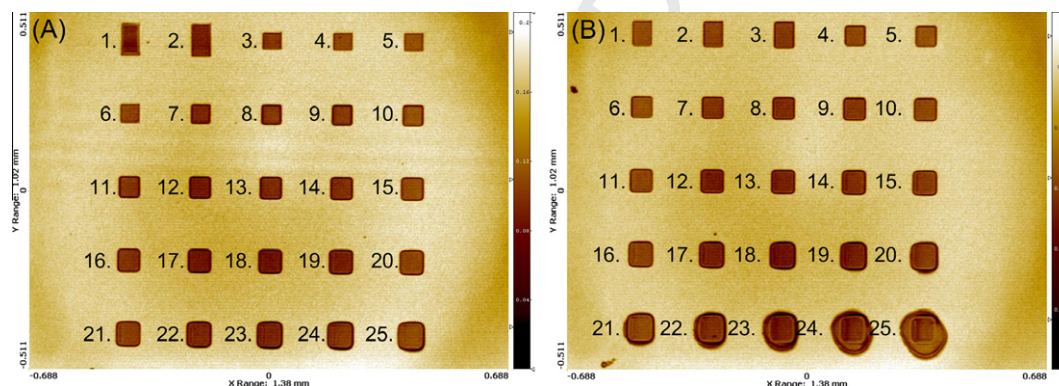


Fig. 2. Topography of PDMS irradiated with dose range (A) 10–10,000 μC/cm² and (B) 50–50,000 μC/cm². The dose increases in a geometric manner with a constant multiplicative factor of 1.33 between subsequent squares. Darker areas denote increasing height.

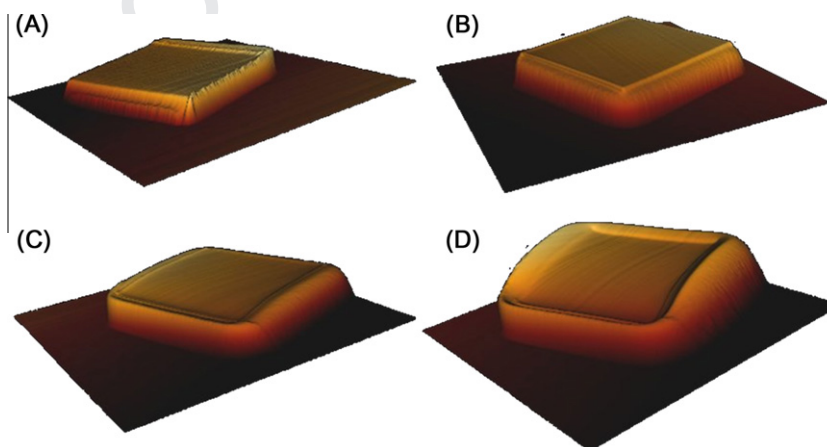


Fig. 3. 3D topology of developed samples after different rates of exposure. The doses are (A) 130 μC/cm², (B) 542 μC/cm², (C) 2.26 mC/cm², and (D) 9.39 mC/cm². The thickness and modulus data are shown in Fig. 4.

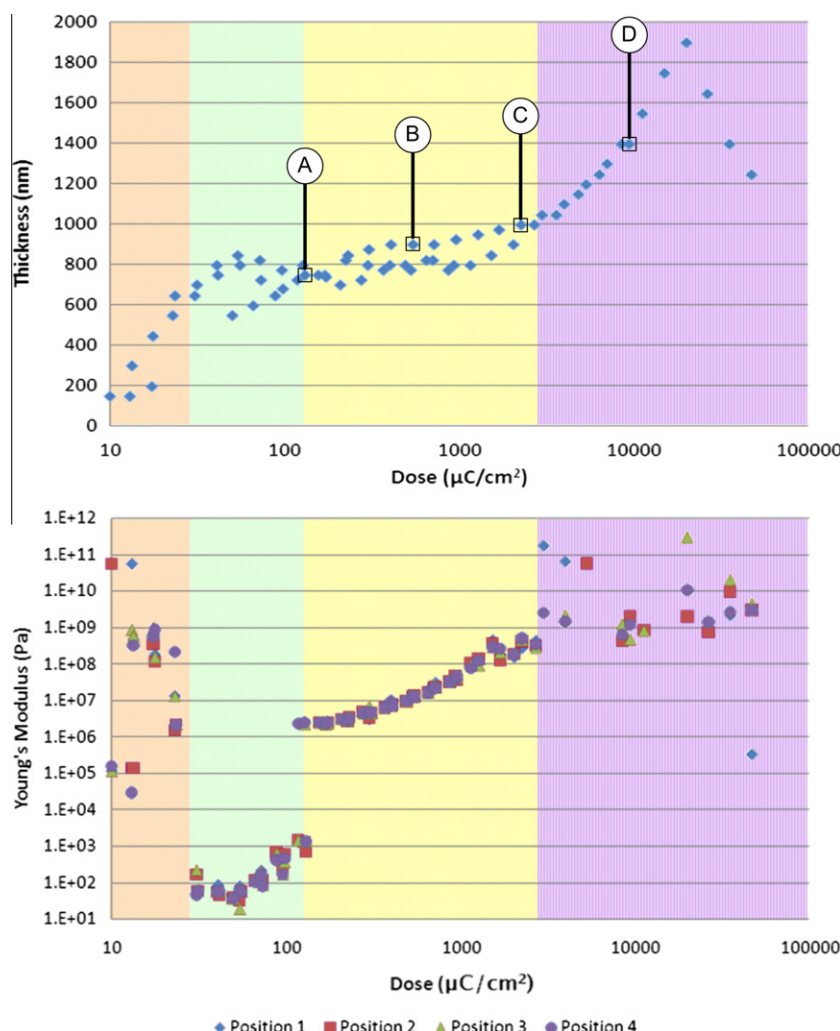


Fig. 4. Effect of dose on (top) retained film thickness and (bottom) Young's modulus. The letters denote the samples which were imaged in Fig. 3.

5 nN during scanning. The results were used to measure the thickness of the PDMS remaining after development.

The data in Fig. 4 shows four distinct regimes corresponding to changes in the phase of the PDMS due to increasing exposure dose. At doses below c.a. $30 \mu\text{C}/\text{cm}^2$ the PDMS is largely removed during development in toluene as denoted by the reduced thickness. The variability in the Young's modulus at these low doses suggests that the remaining film consists largely of a residual aggregate of partially cross-linked polymer chains through which the indentation is affected by the proximity of the substrate. Between $30 \mu\text{C}/\text{cm}^2$ and $150 \mu\text{C}/\text{cm}^2$, the exposed PDMS film appears to be still mostly liquid-like with the apparent increase in elastic modulus most likely corresponding to a change in the viscoelastic properties of the material. It is apparent that cross-linking density is increasing with dose throughout this regime as the amount of PDMS that remains undissolved during development is also increasing. The discontinuity at c.a. $150 \mu\text{C}/\text{cm}^2$ in the Young's modulus data implies a critical cross-linking density at which solidification occurs. At doses above this critical value of $150 \mu\text{C}/\text{cm}^2$, the resultant thickness plateaus to a value close to that of the original liquid film. At doses above c.a. $3000 \mu\text{C}/\text{cm}^2$, there is an increase in the variability in Young's modulus and a steady increase in film thickness above that of the original liquid film thickness. This corresponds to the reduction in resolution as seen in Fig. 2 at higher doses. It is likely that the lateral broadening (i.e. the rounding) of the features, see Fig. 3, is due to backscattering, a well established phenomenon.

The vertical swelling is more likely to be due to high dose enhanced solvent penetration as discussed in [14]. This solvent penetration, which is unlikely to be homogenous over the surface of any particular area, will also cause the variation in the Young's modulus.

4. Conclusions

In this paper the viability of using e-beam lithography to form permanent micro-scale components from thin films of liquid PDMS was investigated. By exposing the PDMS film to a range of doses, it was found that the structure of the resultant film has four distinct phases manifest in both the Young's modulus and remaining thickness after development. In the solid phase it was shown that the Young's modulus can be varied over approximately seven orders of magnitude from that of a viscoelastic material through a rubbery regime to that of a glassy one by controlling the electron dose. At higher doses, excessive backscattering was observed as well as swelling, possibly caused by chain scission resulting in poor spatial resolution.

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